Polymeric Resins Adsorb and Release Oryzalin in Response to pH

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Two polymeric anion-exchange resins and one sorbent resin were evaluated for their propensity to adsorb, and subsequently desorb, oryzalin. The intent was to determine whether these resins could adsorb and subsequently release oryzalin in a manner that would render these resins as an option for slow-release herbicide delivery. The dinitroaniline herbicide oryzalin is weakly acidic with a dissociation constant (pK_a) of 8.6. An additional objective was to determine whether altering the pH between sorption and desorption would enhance the desired performance. Maximum oryzalin sorption by the two anion-exchange resins was between 127 and 132 mg g^{-1} ai. The sorbent resin was adsorbed at a maximum concentration of 191 mg g^{-1} ai. Maximum sorption occurred with the pH 10 solutions with all resins. Average oryzalin desorption by the anion-exchange resin was between 0.12 and 3.84 mg g^{-1} per desorption event. Maximum desorption occurred at pH 6.0. Results reveal that the resins evaluated may have merit for slow-release herbicide delivery.

Nomenclature: Oryzalin.

Key words: Herbicide, adsorption, container-grown plants, nursery.

Oryzalin, one of many dinitroaniline herbicides, was first registered for use in row crop production in 1974 in the United States. Row crop registrations were subsequently canceled in the United States in the 1990s. However, registrations in landscape, container, and field-grown ornamentals and turf products remain essential for PRE weed control in this multibillion dollar industry. Although mulches and fabrics have been investigated for use as weed control in container-grown ornamentals, oryzalin remains essential for economic reasons (Appleton and Derr 1990; Wilen et al. 1999).

Oryzalin is relatively persistent in soil with soil half-life ranges reported from 20 to 128 d (Vencill, 2002). However, soil type and temperature can affect oryzalin longevity (Gingerich and Zimdahl 1976; Graper and Rainey 1989; Krieger et al. 1998). Krieger et al. (1998) determined that oryzalin sorption increased in soils with fine texture, higher cation-exchange capacities, and increasing organic matter content. However, they also reported that the soil-adsorbed fraction of oryzalin and the aqueous soil solution fraction rapidly approached equilibrium. This equilibrium indicates that release from the soil-adsorbed fraction was responsible for the amount of oryzalin in soil solution. However, availability of oryzalin in the soil solution fraction decreased over time because of irreversible adsorption to organic matter.

Studies indicate that oryzalin does not leach through the organic substrate when applied directly into the container during production (Goodwin and Beach 2001). Oryzalin contamination found in containment ponds is due to nontarget losses in runoff water rather than leaching through the pot (Gilliam et al. 1992; Goodwin and Beach, 2001). Wehtje et al. (1994) determined oryzalin adsorption and resistance to leaching was high in organic media. They also determined that oryzalin adsorption was reversible from the organic media back into solution with each irrigation or rainfall event, where it provides control of germinating weed seeds.

Oryzalin is a weak acid and has a dissociation constant (pK_a) of 8.6 (Wauchope et al. 1992). Consequently, oryzalin should be predominately neutral at pH values below 8.6 and anionic at higher values. Oryzalin has an average coefficient of adsorptivity (K_{oc}) of 600 mL g^{-1} (Wauchope et al. 1992) but ranges from 93 to 2,700 ml g^{-1} depending on soil clay and organic content. The high K_{oc} of oryzalin makes it ideal for container plant producers. Studies indicate that high organic content of nursery substrates prevents displacement of herbicides below the top 2 to 4 cm of container medium (Wehtje et al. 1993, 1994, 2000). This characteristic is valuable in preventing leaching into the lower regions of the container where it may cause damage to crop roots or exit the containers into nursery runoff water. Previous research has indicated that the weed control activity of oryzalin increased with increasing soil pH (Robinson 1982). Taking these chemical and other studies about oryzalin soil behavior (Gingerich and Zimdahl 1976; Harvey 1974) into consideration, indications are that oryzalin hysteresis occurs without loss of herbicidal activity.

Many container nurseries apply three to five broadcast applications per year of granular herbicide for PRE weed control (Gilliam et al. 1990). Studies have shown that depending on application equipment, plant species, and container spacing, as much as 86% of applied granular herbicide falls between the containers as nontarget loss (Gilliam et al. 1992; Porter and Parish 1993). It is this nontarget loss that is a major contributing factor to herbicide contamination in nursery runoff. Novel methods of herbicide delivery have been investigated in ornamental container production with varying levels of success. All have been dependent on physical release of the herbicide via dissolving of either tablets (Gorski et al. 1989; Koncal et al. 1981; Verma and Smith 1978), coatings on encapsulated fertilizers (Crossan et al. 1997; Keel et al. 1998), coating on tree bark (Mathers 2003), or impregnated mulches (Fretz 1973) and cellulose materials (Fain et al. 2003). However, none of these methods has been adopted commercially. Typically, extension of weed control beyond a certain time is the main reason for failure, which then results in application of additional herbicide. Use of novel chemical means of delivery has not been thoroughly investigated.

Acidic herbicides are not as strongly adsorbed to soil colloids as basic or nonionic herbicides (Weber, 1970).

Purolite resin	Functional group	Exchangeable ion	AEC	Bulk density	Particle-size distribution	
					>1.2 mm	<0.3 mm
			eq kg^{-1}	g cm^{-1}	%	
A-300	Type I quaternary ammonium	Cl$^-$	3.85	0.84	< 5	< 1
A-400	Dimethylethanolamine	Cl$^-$	3.89	0.75	< 5	< 5
MN-400	Trimethylamine	—[b]	0.60	0.49	< 5	< 5

[a] Abbreviation: AEC, anion-exchange capacity.
[b] MN-400 resin has no exchangeable ion.

However, when disassociated, these herbicides can be reversibly bound to anion-exchange resins by changes in solution pH. This has been demonstrated with bentazon (Abernathy and Wax 1973), imazaquin, imazethapyr (Loux et al. 1989), and sulfentrazone (Grey et al. 2000). As previously described, oryzalin is weakly acidic, with a pK_a of 8.6. Theoretically, oryzalin could be reversibly bound to an anion-exchange resin and then with subsequent irrigation or rainfall, desorption should occur. If possible, this chemical method of herbicide delivery could provide adequate season-long herbicidal activity in ornamental containment operations. Although the weed control potential of this method has been evaluated in one study (Fain et al. 2003), the principle for the method has not been described.

To better understand the adsorption and desorption behavior of oryzalin, laboratory studies examined the electrical charge characteristics of this herbicide and the effect of pH using different forms of exchange resins. The first hypothesis was that the oryzalin molecule, in either the neutral or anionic form, may have charged regions that would facilitate adsorption to resins. This would be accomplished through computer modeling. Our second hypothesis was that oryzalin could be adsorbed to anionic resins at a pH greater than 8.6. Our third hypothesis was that the desorption rate and availability of oryzalin from anion resins respond to repeated wetting events and to pH.

Materials and Methods

Computer Modeling. Semiempirical Austin Model 1 (AM1) (Dewar et al. 1985) calculations were performed with SPARTAN[1] Software on a Silicon Graphics Indego[2] R10000 graphic-accelerated workstation. These calculations were used to model the location and degree of positive and negative charges on the oryzalin molecule in the neutral and anionic form. A detailed description of the theoretical basis and hardware requirements have been described previously (Dayan et al. 1998; Grey et al. 2000). This model portrays a given molecular structure in its most logical configuration in a three-dimensional context. Based on that configuration, electron density across the topography of the oryzalin molecule was calculated and portrayed colorimetrically. Resulting electrostatic potentials allowed us to identify sites on the oryzalin molecule of electrophillic attraction, which could occur when in the anionic form. Our intent was to determine the theoretically possibility of oryzalin having sufficiently charged regions to permit coulombic-based attraction to exchange resins.

Exchange Resins. Three ion-exchange resins (Table 1) and two pH solutions were used to empirically determine the

adsorption of oryzalin using a procedure previously described by Grey et al. (2000). Resins were selected to provide varying levels of anion adsorption (Purolite A-300[3] [Anonymous 1998a] and Purolite A-400[3] [Anonymous 1998b]) and nonchemical adsorption (Purolite MN-400[3] [Anonymous 1998c]). Purolite A-300 and A-400 anion-exchange resins, both made of polymer matrix structures of polystyrene cross-linked with divinylbenzene, have functional groups of type I quaternary ammonium and dimethylethanolamine, respectively. Both resins have chloride as the ionic form. Total exchange capacity for the A-300 and A-400 are 3.85 and 3.89 eq kg^{-1} dry weight, respectively. Purolite MN-400 sorbent resin is made of highly and rigidly cross-linked polystyrene, characterized by a very high internal surface area of 800 to 1000 m^2 g^{-1} and a pore volume of 1.0 to 1.1 ml g^{-1}. The functional group of the MN-400 resin is trimethylamine. Total exchange capacity for the MN-400 was 0.6 eq kg^{-1}. The capacity of each resin to adsorb oryzalin was tested when placed in various concentrations of oryzalin that had been buffered to either pH 7.0 or 10.0. Adsorption and desorption were studied separately.

Adsorption Experiments. ^{14}C-oryzalin stock solution was prepared by adding 48.47 kBq of ^{14}C-oryzalin[4] to 200 µl of methanol and, then, diluting with 800 µl of deionized water. Solutions of pH 7.0, buffered with monobasic potassium phosphate and sodium hydroxide, and pH 10.0, buffered with boric acid, potassium chloride, and sodium hydroxide, were prepared from certified concentrates.[5] Fifty milliliters of each buffer solution were placed in each of eight (four for each pH treatment) 200-ml glass beakers, and 100 µl of ^{14}C-oryzalin stock solution was added to each beaker. Commercially formulated oryzalin (Surflan)[2] was added to each beaker to yield concentrations of 0, 0.1, 1.0, and 10.0 g L^{-1}. Three subsamples of 250 µl were removed from each beaker for ^{14}C-oryzalin quantification using liquid-scintillation spectrometry (LSS).[6] That value served as a baseline for later comparison. Liquid scintillators emit light in the blue region of the spectrum. Oryzalin is a bright-orange crystalline powder that adds significant color in the yellow spectrum to the samples, causing color quenching, which results in reduced counting efficiency. Therefore, before counting samples containing oryzalin, counting correction with color-quenched standards was performed to establish quench parameters and a quench curve.

Sample of 1 g (dry weight) of each resin were placed into 20-ml high-density polyethylene (HDP) scintillation vials,[5] and 5 ml of each solution was added to three HDP vials containing the resins. Vials were arranged horizontally on an Eberbach model 6000[7] reciprocal platform shaker and agitated at a consistent speed for 24 h at 180 cycles per

minute with a horizontal stroke of 3.81 cm. Subsequently, two 250-µl subsamples were immediately removed from each vial and placed in clean HDP vials along with 15 ml of ScintiSafe Econo 1 scintillation cocktail.[5] Vials were then analyzed for ^{14}C-oryzalin content using LSS. Any decrease in radioactivity in that value relative to the previous quantification was attributed to resin adsorption. There were a total of 24 treatments (two pH values, three resins, and four oryzalin concentrations). A completely randomized design with three replications per treatment was used. A second similar experiment was conducted using the same procedures, except oryzalin concentrations were 1, 10, 20, and 40 g L^{-1}.

Data from the adsorption experiment were analyzed using Tukey's honest significant difference test (5% level) to determine response between resins at a given pH and oryzalin concentration, as well as response between pH values, for each resin and oryzalin concentration. ANOVA revealed no differences between repeated experiments; therefore, pooled data are presented.

Desorption Experiments. Two desorption experiments simulated release of oryzalin from the resins by wetting events. In the first experiment, 5 g of each resin were loaded with ^{14}C-oryzalin using the pH 10.0 solution at a concentration of 10 g L^{-1} oryzalin. Loading procedures were as previously described, and 0.5 g of oryzalin–resin formulation was placed into 60-ml cylindrical separatory funnels; glass wool was placed below the resin to prevent loss of resins during wetting events. Remaining oryzalin–resin formulations were placed in sealed HDP vials for a subsequent replication of this experiment. To facilitate desorption, 3 ml of deionized water was added daily, allowed to remain for 30 min, then drained into glass beakers. Funnels were sealed after draining to maintain moisture level and avoid resin shrinkage between daily events. A 200-µl subsample of the drained liquid was collected and analyzed for ^{14}C-oryzalin content as previously described. A completely randomized design with four replications was used. ANOVA revealed no differences between repeated experiments; therefore, pooled data are presented.

Data for the first desorption experiment were analyzed using linear regression to determine response over time for each resin. Confidence intervals (1% level) were calculated for the slope parameter of each resin to determine whether there was a difference in release rate for each resin (Rao 1998).

In the second experiment, 0.5-g samples of oryzalin–resin formulation were placed into 60-ml cylindrical separatory funnels; glass wool placed below the resin prevented resin loss. Oryzalin-loaded resin samples were leached with a solution that had been buffered to a pH of 6.0, 8.0, or 10.0. The pH 6.0 solution was buffered with potassium phosphate and monobasic disodium phosphate, the pH 8.0 solution was buffered with potassium phosphate and monobasic sodium hydroxide, and the pH 10.0 solution was buffered with boric acid, potassium chloride, and sodium hydroxide. All buffer solutions were prepared from certified concentrates.[3] Three milliliters of the appropriate buffer solutions were added daily, allowed to remain for 30 min, and then drained into glass beakers. Funnels were sealed after draining to maintain moisture level and avoid resin shrinkage between simulations. Drained liquid was collected and analyzed for ^{14}C-oryzalin content.

This experiment was also repeated, and the pooled data were analyzed together in a two-by-three factorial, repeated-measures design, with experiment and pH by experiment as

between-subject effects and all other effects as within-subject effects. Inspection of the ANOVA table (not shown) revealed a significant pH by experiment by event effect (P < 0.0001), which means that the time profiles of the three pH treatments varied by experiment or that the pH-by-event interaction varied by experiment. After observing that interaction, subsequent analyses were conducted using averages over events 1 to 10, 11 to 20, and 21 to 30, as response variables. Inspection of the ANOVA table (not shown) showed that a repeated-measures approach was no longer necessary because the process of taking averages completely diminished the serial correlation within funnels. That is, the random effect of the funnel nested within the treatment was not significant (P = 0.3227). Therefore, subsequent analyses were based on fixed effects of a 3 by 3 by 2 factorial design with pH, event, and experiment as the experimental factors. Comparisons among treatments were made within each of the two replications. LSDs were calculated using Bonferroni adjustment to account for multiplicity of comparisons ($k = 18$) while holding the experimentwise error rate at $\alpha = 0.05$, and using variance components estimated from the combined data from both experiments (Rao 1998).

Results and Discussion

Computer Modeling. To analyze quantitatively the relative charge patterns or positive and negative regions (Figures 1 and 2) in a non-pH–based scenario electrostatic potential on the electron-density isosurface was calculated. As expected, the entire outer surface of the molecule of ionized oryzalin was highly electronegative. This high electronegativity occurs at pH values above the pK_a of oryzalin, and thus, explains the greater affinity for adsorption with the pH 10.0 solutions (Tables 2 and 3).

Adsorption Experiments. Adsorption varied with pH (Tables 2 and 3). In the first experiment all three resins, adsorbed oryzalin was in excess of 94% in the pH 10 solution, regardless of oryzalin concentration. Percentage of oryzalin adsorbed was 93.2, 92.4, 84.8, and 47.5% at 0.0, 0.1, 1.0, and 10.0 g L^{-1} oryzalin, respectively for the A-300 resin at pH 7.0. Adsorption was similar for the A-400 resin at pH 7.0 with adsorption dropping to 42.4% at 10.0 g L^{-1} oryzalin.

There was no difference in percentage of oryzalin adsorbed between resins with any oryzalin solution concentration, except 1 g L^{-1} pH 7.0 solution, where the percentage of oryzalin adsorbed was 84.8 and 82.4% for the A-300 and A-400 resins, respectively, compared with 93.8% for the MN-400 resin (Table 2). Similarly, for the 10 g L^{-1} pH 7.0 solution, percentage of oryzalin adsorbed dropped from 95.4% for the MN-400 resin to 47.5 and 42.4% for the A-300 and A-400 resins, respectively. When pH was contrasted for each resin at each oryzalin solution concentration, the pH 10.0 solutions yielded the highest percentage of adsorption for all contrasts, except for the MN-400 resin at 10 g L^{-1} oryzalin (Table 2).

In the second adsorption experiment, there was no difference in percentage of oryzalin adsorbed at pH 10 between resins for the 1 and 10 g L^{-1} solutions; however, with the 20 and 40 g L^{-1} solutions, the percentage of oryzalin adsorbed was less for the A-300 and A-400 resins compared with the MN-400 resin (Table 3). At 20 g L^{-1}

Figure 1 (structures)

neutral form

H3C 0.03 — 0.02 CH2 — 0.0 H2C — CH3 0.03
H2C 0.17 — N -0.38
-0.33 O / N 0.53 / O -0.33
0.27
-0.18
0.28
-0.32 O / N 0.54 / O -0.32
0.22 CH2
-0.14
0.27
-0.44
-0.64 O=S=O -0.63
1.47
NH2
-0.09

(ΔH = -43.698 kcal/mol)

anionic form

H3C 0.0 — 0.01 CH2 — 0.0 H2C — CH3 0.0
H2C 0.16 — N -0.38
-0.35 O / N 0.52 / O -0.37
0.19
-0.17
0.24
-0.35 O / N 0.53 / O -0.36
0.20 CH2
-0.14
0.24
-0.42
-0.77 O=S=O -0.71
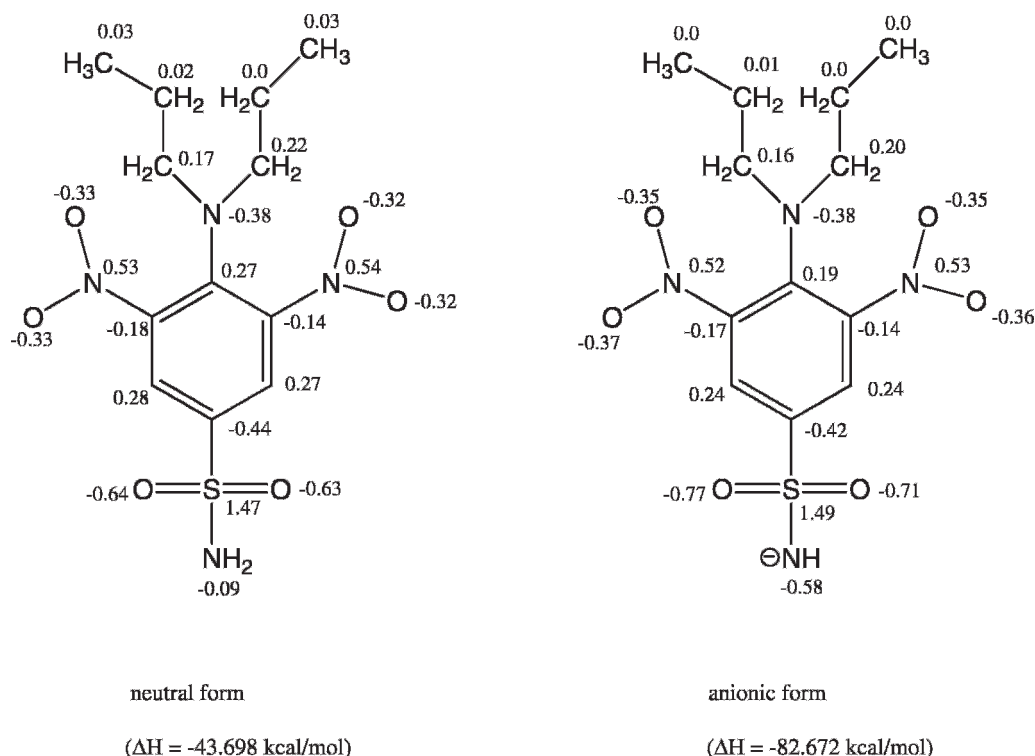1.49
⊖NH
-0.58

(ΔH = -82.672 kcal/mol)

Figure 1. Calculated electrostatic potentials on the electron density isosurface of oryzalin in a neutral and anionic form (ΔH = change in enthalpy).

oryzalin, at pH 10, the amount of oryzalin adsorbed was 89.7% for the MN-400 resin compared with 72.0 and 72.4% for the A-300 and A-400 resins, respectively. At pH 7.0, the MN-400 resin adsorbed the greatest amount of oryzalin across all concentrations, and there was no difference in oryzalin adsorbed at pH 7.0 for the A-300 or A-400 resin at any solution concentration. The greatest percentage of oryzalin was adsorbed using the pH 10.0 solution across all resins and concentrations (Table 3).

Desorption Experiments. In the first experiment, after 30 simulated irrigations, the A-400, A-300, and MN-400 resins had released 9.2, 6.0, and 1.7% of the adsorbed oryzalin, respectively (Figure 3). Leaching was continued for 27 more events; however, there was no difference in amount of release

for any resin (data not shown). Thus, after 57 wetting events, the A-400, A-300, and MN-400 resins had released 11.7, 8.7, and 3.3% respectively.

In the second experiment, oryzalin desorption was affected by solution pH as well as by wetting events (Table 4). These results confirmed the speculation that using water with pH above the pK_a of oryzalin would result in limited oryzalin desorption because of the high electronegativity of oryzalin in its anionic state.

During the first 10 events, pH 6.0 and 8.0 solutions released more oryzalin, with average amount released ranging from 0.67 to 1.92% per event (Table 5). During events 11 to 20, the pH 6.0 solution continued to desorb more oryzalin than the pH 10.0 solution. During events 21 to 30, the pH 8.0 solution desorbed more than the pH 10.0 for the first
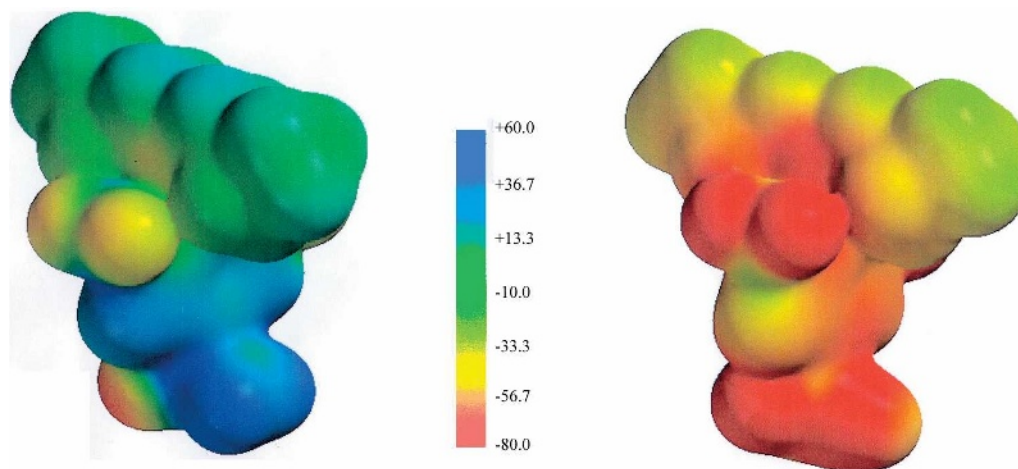
Figure 2. Computer-based estimation of the electrostatic potential of the molecular surface of oryzalin as a (left image) neutral and (right image) anionic form. Cool colors represent positive potential with blue representing +60 kcal mol^{-1}. Warm colors represent negative potential with red representing —80 kcal mol^{-1}.

Table 2. Percentage of oryzalin adsorption with two anion-exchange (A-300 & A-400) and one sorbent (MN-400) resin affected by solution pH and oryzalin concentration (experiment 1).[a,b]

	0^c mg L^{-1}		100 mg L^{-1}		1,000 mg L^{-1}		10,000 mg L^{-1}	
Resin	pH 7	pH 10	pH 7	pH 10	pH 7	pH 10	pH 7	pH 10
				% of available				
MN-400	91.4 b B	93.9 a A	92.9 a B	95.2 a A	93.8 a B	95.5 a A	95.4 a A	95.2 a A
A-300	93.2 a B	95.3 a A	92.4 a B	95.0 a A	84.8 b B	95.1 a A	47.5 b B	94.3 b A
A-400	92.1 ab B	93.9 a A	90.9 b B	94.9 a A	82.4 b B	95.1 a A	42.4 b B	94.2 b A

[a] Means followed by same lowercase letter within columns do not differ significantly according to Tukey's HSD ($P < 0.05$).
[b] Means followed by same uppercase letter within rows for a fixed oryzalin concentration do not differ significantly according to Tukey's HSD ($P \leq 0.05$).
[c] The 0 mg L^{-1} concentration represents only the ^{14}C-oryzalin; The actual concentration was 0.07 ppb.

Table 3. Percentage of oryzalin adsorbed with two anion-exchange resins (A-300 & A-400) and one sorbent resin (MN-400) affected by solution pH and oryzalin concentration (experiment 2).[a,b]

	1,000 mg L^{-1}		10,000 mg L^{-1}		20,000 mg L^{-1}		40,000 mg L^{-1}	
Resin	pH 7	pH 10	pH 7	pH 10	pH 7	pH 10	pH 7	pH 10
				% of available				
MN-400	96.4 a B	99.1 a A	97.4 a B	99.7 a A	87.8 a A	86.7 a A	95.3 a A	81.3 a B
A-300	88.5 b B	98.5 a A	63.8 b B	99.1 a A	55.8 b B	71.9 b A	47.5 b B	63.7 b A
A-400	87.2 b B	98.8 a A	59.2 b B	99.6 a A	49.1 b B	72.4 b A	42.4 b B	66.2 b A

[a] Means followed by same lowercase letter within columns do not differ significantly according to Tukey's HSD ($P < 0.05$).
[b] Means followed by same uppercase letter within rows for a fixed oryzalin concentration do not differ significantly according to Tukey's HSD ($P \leq 0.05$).

replication; however, for the second replication, the pH 6.0 solution exhibited more desorption. It is this switch in the amount of desorption between pH 6.0 and 8.0 solutions during events 21 to 30 that accounts for the experiment and time interactions (Table 2). This work adds to the previous work by Fain et al. (2003) and provides further understanding of the behavior of oryzalin with anion-exchange resins. The maximum amount of oryzalin desorbed after 30 simulated irrigations was 26.8%. In comparison, Keese et al. (1994) reported that the release of oryzalin from the granular formulation Rout was comparatively rapid, with cumulative loss after 21 simulated irrigations of 71.3%.

Results of these experiments indicate that anion-exchange resins may have potential as extended-delivery carriers of oryzalin and, perhaps, other PRE-active herbicides. Should exchange resins be developed as extended-delivery carriers of oryzalin and, perhaps, other PRE-active herbicides, the information presented here may aid in predicting their behavior under conditions in which the pH of irrigation water varies.
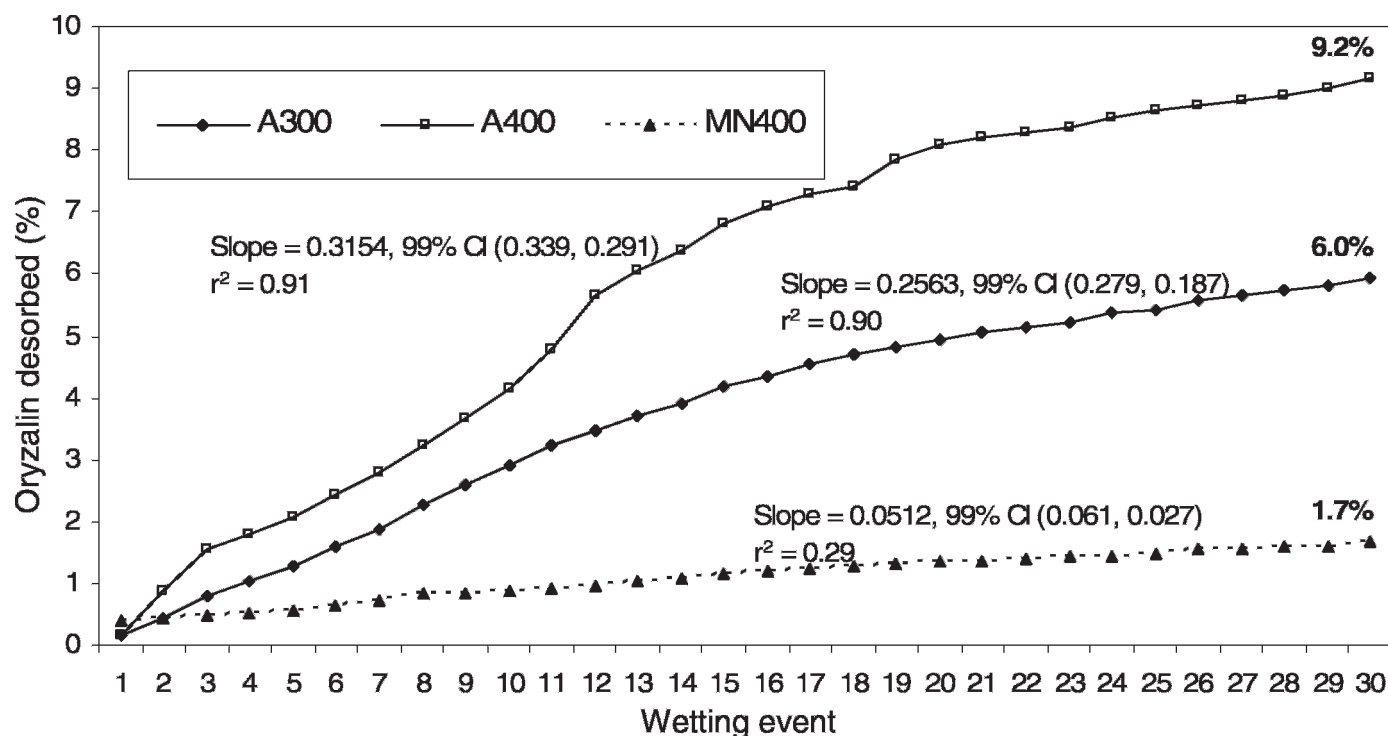

Figure 3. Effects of wetting events on oryzalin desorption over time.

Table 4. ANOVA results for oryzalin desorption from anion-exchange resins at pH 6.0, 8.0, and 10.0.[a]

Source	DF	Sum of squares	Mean square	F value	Pr > F
Model	17	14.098	0.829	25.58	< 0.0001
Error	39	1.265	0.032		
Corrected total	56	15.363			
$R^2 = 0.92$					

Source	DF	Type III SS	Mean square	F value	Pr > F
pH	2	6.4889	3.2445	100.06	< 0.0001
Event	2	4.0932	2.0466	63.12	< 0.0001
pH × event	4	2.2692	0.5673	17.50	< 0.0001
Experiment	1	0.0067	0.0067	0.21	0.6513
pH × experiment	2	0.0892	0.0446	1.38	0.2646
Experiment × time	2	0.0410	0.0205	0.63	0.5367
pH × experiment × time	4	1.2623	0.3156	9.73	< 0.0001

[a] Abbreviation: DF, degrees of freedom; SS, sum of squares.

Development of a controlled delivery herbicide that could be applied directly to individual nursery containers would be a beneficial best-management practice for container plant production. Such a product could greatly reduce the number of herbicide applications needed for weed control or reduce or eliminate nontarget herbicide loss, thereby, improving nursery runoff water quality. This study investigates novel materials that might have the potential to be developed into such a product.

Sources of Materials

[1] SPARTAN version 5.0, Wavefunction, Inc. 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.

[2] Silicon Graphics INDIGO2 R10000 graphics-accelerated workstation, Silicon Graphics, Inc., 2011 North Shoreline Boulevard, Mountain View, CA 94039.

Table 5. Effect of solution pH on oryzalin desorption with Purolite A-400 anion-exchange resin.

	Number of wetting events[a]		
Experiment	1 to 10	11 to 20	21 to 30
Experiment 1			
pH 10.0 ($n = 4$)	0.07	0.06	0.06
pH 8.0 ($n = 3$)	0.67	0.53	0.64
pH 6.0 ($n = 3$)	1.92	0.57	0.38
Contrasts			
10.0 vs. 8.0 (LSD = 0.439)[b]	*	*	*
8.0 vs. 6.0 (LSD = 0.469)	*	NS	NS
10.0 vs. 6.0 (LSD = 0.439)	*	*	NS
Experiment 2			
pH 10.0 ($n = 3$)	0.23	0.06	0.05
pH 8.0 ($n = 3$)	1.24	0.37	0.25
pH 6.0 ($n = 3$)	1.35	0.53	0.60
Contrasts			
10.0 vs. 8.0 (LSD = 0.469)	*	NS	NS
8.0 vs. 6.0 (LSD = 0.469)	NS	NS	NS
10.0 vs. 6.0 (LSD = 0.469)	*	*	*

[a] Average percentage of oryzalin desorbed per wetting event for events 1 to 10, 11 to 20, and 21 to 30.
[b] LSDs were calculated using Bonferroni adjustment to account for multiplicity of comparisons ($k = 18$), and using variance components estimated from the combined data from both experiments.
* Significant at P ≤ 0.05.

Acknowledgments

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